

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 747 430 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
**29.03.2000 Bulletin 2000/13**

(51) Int Cl.7: **C08L 23/00, C08L 23/10**

(21) Application number: **96109107.1**

(22) Date of filing: **07.06.1996**

(54) **Reactor blends of small amounts of syndiotactic polypropylene in isotactic polypropylene**

Reaktormischungen aus kleinen Mengen syndiotaktischem Polypropylen in isotaktischem Polypropylen

Mélanges de petites quantités de polypropylène syndiotactique avec polypropylène isotactique dans un réacteur

(84) Designated Contracting States:  
**BE DE ES FR GB IT NL**

(30) Priority: **07.06.1995 US 475315**

(43) Date of publication of application:  
**11.12.1996 Bulletin 1996/50**

(73) Proprietor: **FINA TECHNOLOGY, INC.**  
**Plano, Texas 75024 (US)**

(72) Inventors:  
• **Shamshoum, Edwar S.**  
**Houston, Texas 77062 (US)**  
• **Reddy, Balreddy R.**  
**Baytown, Texas 77520 (US)**

• **Palz, Rolando**  
**Guatemala City, C.P. 01014 (GT)**  
• **Goins, Michael J.**  
**Houston, Texas 77089 (US)**

(74) Representative: **Leyder, Francis et al**  
**c/o Fina Research S.A.**  
**Dept. Brevets**  
**Zone Industrielle C**  
**7181 Seneffe (Feluy) (BE)**

(56) References cited:  
**EP-A- 0 536 104**  
  
• **DATABASE WPI Derwent Publications Ltd.,**  
**London, GB; AN 95-237198 XP002014138 &**  
**JP-A-07 145 202 (MITSUI TOATSU), 6 June 1995**

**EP 0 747 430 B1**

*AE*

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**Description****SPECIFICATION**5 **BACKGROUND OF THE INVENTION**

[0001] **FIELD OF THE INVENTION:** This invention relates to a polymer blend, specifically, to a reactor blend of polypropylenes having different microstructures, i.e., a reactor blend of isotactic polypropylene and syndiotactic polypropylene and a process for making such a blend having increased molecular weight distribution, improved clarity, higher melt flow and higher xylene solubles.

**DESCRIPTION OF THE PRIOR ART:**

[0002] It is known that two or more homogeneous catalysts, such as those based on metallocene compounds, may be combined to effect properties, such as molecular weight distribution. U.S. Patent No. 4,530,914 discloses use of a catalyst system comprising two or more metallocenes in the polymerization of  $\alpha$ -olefins, primarily ethylene, to obtain a broad molecular weight distribution. The metallocenes each have different propagation and termination rate constants. The metallocenes are mixed with an alumoxane to form the catalyst system.

[0003] It is known that blends of isotactic and syndiotactic polypropylene can be formed with a Ziegler polymerization catalyst as described in Belgian Patent 538,782. As disclosed in U.S. Patent No. 3,268,627, a mixture of from about 50-97% by weight of isotactic polypropylene and from about 3-50% by weight of a syndiotactic polypropylene can be formed with up to about 20% by weight of atactic polypropylene.

[0004] It is also known to produce polymer blends by polymerizing two or more polymerizable materials in two or more reactors arranged in series. As disclosed in U.S. Patent No. 4,937,299, a polymerizate is produced in a first reactor and then the first polymerizate is passed to a second reactor wherein a second polymerizate is produced thereby obtaining a blend of the first and second polymerizates.

[0005] It is also known to produce a reactor blend of polyolefins in a single reactor by use of a homogeneous catalyst system comprising at least two different metallocenes and an alumoxane. As disclosed in U.S. Patent No. 4,937,299, two different metallocenes can polymerize ethylene and propylene to form an ethylene-propylene copolymer in a single reactor.

[0006] It would be advantageous to provide a process to produce a polymer blend of isotactic polypropylene and syndiotactic polypropylene having improved properties over both homopolymers. Furthermore, it would be advantageous to provide a polymer blend which could be produced in a single reactor.

35 **SUMMARY OF THE INVENTION**

[0007] Accordingly, this invention provides a reactor blend of isotactic polypropylene and syndiotactic polypropylene.

[0008] And, an object of this invention is to provide a polymer blend of isotactic polypropylene and syndiotactic polypropylene in a single reactor.

[0009] Also, an object of this invention is to provide a polymer blend having up to 4% by weight of syndiotactic polypropylene to produce increased molecular weight distribution.

[0010] Further, an object of this invention is to provide a polymer blend having up to 13.9% by weight of syndiotactic polypropylene to improve the clarity or haze of biaxially oriented film.

[0011] Additionally, an object of this invention is to provide a polymer blend having from 2.34% by weight of syndiotactic polypropylene to 13.9% by weight and a melt flow higher than that for either a syndiotactic homopolymer or an isotactic homopolymer.

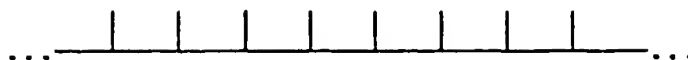
[0012] As well, an object of this invention is to provide a polymer blend having from 2% by weight of syndiotactic polypropylene to 13.9% by weight and a level of xylene solubles that is higher than that for either a syndiotactic homopolymer or an isotactic homopolymer.

[0013] These and other objects are accomplished by use of at least one homogeneous catalyst and at least one heterogeneous catalyst, preferably in a single reactor.

**DETAILED DESCRIPTION OF THE INVENTION**

[0014] Olefins, especially propylene, may be polymerized to form polyolefins in amorphous (atactic) or crystalline forms. Examples of crystalline forms are isotactic and syndiotactic.

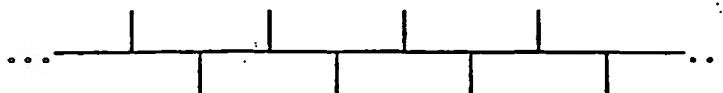
[0015] Isotactic polypropylene contains principally repeating units with identical configurations and only a few erratic, brief inversions in the chain. Isotactic polypropylene may be structurally represented as



The methyl groups attached to the tertiary carbon atoms of successive monomeric units on the same side of a hypothetical plane through the main chain of the polymer, e.g., the methyl groups are all above or below the plane.

[0016] Another way of describing the structure is through the use of NMR. Bovey's NMR nomenclature for an isotactic pentad is ...mmmm... with each "m" representing a "meso" dyad or successive methyl groups on the same side in the plane. As known in the art, any deviation or inversion in the structure of the chain lowers the degree of isotacticity and crystallinity of the polymer.

[0017] A syndiotactic polymer contains principally units of exactly alternating stereoisomers and is represented by the structure:



The methyl groups attached to the tertiary carbon atoms of successive monomeric units in the chain lie on alternate sides of the plane of the polymer.

[0018] In NMR nomenclature, this pentad is described as ...rrrr... in which each "r" represents a "racemic" dyad, i.e., successive methyl groups on alternate side of the plane. The percentage of r dyads in the chain determines the degree of syndiotacticity of the polymer. Syndiotactic polymers are crystalline and like the isotactic polymers are insoluble in xylene. This crystallinity distinguishes both syndiotactic and isotactic polymers from atactic polymer that is soluble in xylene.

[0019] A polymer chain showing no regular order of repeating unit configurations is an atactic polymer. In commercial applications, a certain percentage of atactic polymer is typically produced with the crystalline form. One indication of the amount of atactic polymer is amount of polymer soluble in hot xylene (xylene solubles).

[0020] A multi-catalyst system for the polymerization of propylene in which separate polymerizations with a homogeneous catalyst and with a heterogeneous catalyst are possible. Preferably, the multi-catalyst system is useful in the polymerization of olefins, more preferably,  $\alpha$ -olefins, and, most preferably, propylene. This catalyst system is disclosed in U.S. Serial No. 776,498 filed October 11, 1991.

[0021] A multi-catalyst system of the present invention is obtained by mixing the components of at least one metallocene catalyst and at least one conventional supported Ziegler-Natta catalyst. Generally, the components of a metallocene catalyst are a metallocene compound and an ionizing agent. Generally, the components of a conventional supported Ziegler-Natta catalyst are an aluminum alkyl and a transition metal compound with, optionally, an electron donor.

[0022] Any of the conventional heterogeneous Ziegler-Natta transition metal compound catalyst components for producing isotactic polyolefins can be used in the present invention. The compound is preferably of the general formula  $MR^+_x$  where M is the metal,  $R_+$  is a halogen or a hydrocarboxyl and x is the valence of the metal. Preferably, M is a Group IVB, VB or VIB metal, more preferably a Group IVB, and most preferably titanium. Preferably,  $R^+$  is chlorine, bromine, an alkoxy or a phenoxy, more preferably chlorine or ethoxy and most preferably, chlorine. Illustrative examples of the transition metal compound catalyst components are  $TiCl_4$ ,  $TiBr_4$ ,  $Ti(OC_2H_5)_3Cl$ ,  $Ti(OC_2H_5)Cl_3$ ,  $Ti(OC_4H_9)_3Cl$ ,  $Ti(OC_3H_7)_2Cl_2$ ,  $Ti(OC_6H_{13})_2Cl_2$ ,  $Ti(OC_2H_5)_2Br_2$  and  $Ti(OC_{12}H_{25})Cl_3$ . Mixtures of the transition metal compounds may be used. No restriction on the number of transition metal compounds is made as long as at least one transition metal compound is present.

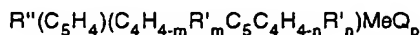
[0023] The transition metal compound is supported on an inert solid which is chemically unreactive with any of the components of the heterogeneous or homogeneous catalyst. The support is preferably a magnesium compound. Examples of the magnesium compounds which are to be used to provide a support source for the catalyst component are magnesium halides, dialkoxymagnesiums, alkoxymagnesium halides, magnesium oxyhalides, dialkylmagnesiums, magnesium oxide, magnesium hydroxide, and carboxylates of magnesium.

[0024] The aluminum alkyl is of the general formula  $AlR^{\#}_3$  where  $R^{\#}$  is an alkyl of from 1-8 carbon atoms and  $R^{\#}$  may be the same or different. Examples of aluminum alkyls are trimethyl aluminum (TMA), triethyl aluminum (TEAL) and triisobutyl aluminum (TiBAI). The preferred aluminum alkyl is TEAL.

[0025] The electron donor is any one of the electron donors which are effective with conventional supported Ziegler-

Natta catalysts. Typically, an electron donor is an organosilicon compound. Examples of electron donors are cyclohexylmethyltrimethoxysilane (CMS), diphenyldimethoxy silane (DPMS) and isobutyltrimethoxy silane (IBMS). Other examples of electron donors are disclosed in U.S. Patent Nos. 4,218,339; 4,395,360; 4,328,122; 4,473,660; 4,562,173 and 4,547,552.

**[0026]** The metallocene catalyst is formed from a neutral metallocene compound, i.e., a metal derivative of a cyclopentadiene. The metallocene compound useful in the present invention contains two cyclopentadiene rings and is of the general formula:



wherein  $(C_5H_4)$  is a cyclopentadienyl ring and  $(C_4H_4-mR'_mC_5C_4H_4-nR'_n)$  is a substituted cyclopentadienyl ring preferably, a fluorenyl ring or a substituted fluorenyl ring, the substituent preferably being alkyl, alkoxy, dialkylamino, halogens, cycloalkyl or aryl;  $R'$  is a hydrocarbyl radical, halogen, an alkoxy, an alkoxy alkyl or an alkylamino radical having from 1-20 carbon atoms, each  $R'$  may be the same or different;  $R''$  is a structural bridge between the  $(C_5H_4)$  and  $(C_4H_4-mR'_mC_5C_4H_4-nR'_n)$  rings to impart stereorigidity and, preferably, is an alkylene radical having 1-4 carbon atoms, or arylalkyl or diaryl alkyl radical contains 7-20 atoms, a silicon hydrocarbyl compound, a germanium hydrocarbyl compound, an alkyl phosphine, or an alkyl amine;  $Q$  is a hydrocarbon radical, such as an alkyl, aryl, alkenyl, alkylaryl or arylalkyl radical having 1-20 carbon atoms, or is a halogen;  $Me$  is a Group IIIB, IVB, VB, or VIB metal as positioned in the Periodic Table of Elements;  $0 \leq m \leq 4$ ;  $0 \leq n \leq 4$ ; and  $p$  is the valence of  $Me$  minus 2.

**[0027]** The cyclopentadienyl rings  $(C_5H_4)$  and  $(C_4H_4-mR'_mC_5C_4H_4-nR'_n)$  must have bilateral or pseudo-bilateral symmetry. Bilateral symmetry is defined as the condition in which there is no substituents or one or more substituents on one side and no substituents or one or more substituents on the other side in the same relative position such that a mirror image is formed from one side to another. Pseudobilateral symmetry is defined as symmetry such that a mirror image exists from one side to the other in regard to the existence and position of substituents but the substituents themselves are not identical.

**[0028]** The metallocene catalyst is syndiotactic specific or syndiospecific. Such catalyst are described in U.S. Patents Nos. 4,895,851; 5,162,278; 5,155,080; 5,132,381 and European Patent Application Publication Nos. 0 387 609; 0 387 690; 0 387 691; and PCT International Publication No. WO 92/1218.

**[0029]** The ionizing agent is an alumoxane, an aluminum alkyl, other Lewis acid or a combination thereof which will ionize a neutral metallocene compound to form a cationic metallocene catalyst. An example of an ionizing agent useful in the present invention is methylalumoxane (MAO).

**[0030]** Reactor blends for purposes of this invention are mixtures of two different microstructures of polypropylene having different physical properties which are produced together in a single polymerization reactor. Catalysts employed in the production of such a polymer blend under steady state conditions in one reactor will comprise two or more distinct catalysts, one predominately catalyzing the formation of one microstructure of polypropylene and the other predominately catalyzing the formation of the other microstructure of polypropylene.

**[0031]** The blends of the present invention are of isotactic polypropylene and syndiotactic polypropylene. Varying the level of syndiotactic polypropylene affects the molecular weight distribution, the clarity or haze of biaxially oriented film, melt flow and xylene solubles.

**[0032]** The invention having been generally described, the following examples are given as particular embodiments of the invention and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims to follow in any manner.

#### PREPARATION OF SUPPORTED METALLOCENE CATALYST

**[0033]** Under nitrogen, a slurry of dry silica in dry toluene is treated with methylalumoxane (MAO) dissolved in toluene while keeping the MAO/silica weight ratio at about 0.2-1.0. The mixture is heated under reflux for four hours and the liquid is decanted. The solid is washed with several portions of toluene and dried. Under nitrogen, metallocene dissolved in toluene is added to a slurry of MAO treated silica in toluene (2-10% by weight of metallocene based on the MAO treated silica). Upon completion of the reaction, the solid is isolated and washed further with hexane and dried. When a syndiospecific metallocene is used, a purple solid is obtained. The solid is stored under an inert atmosphere and away from light. The ratio of metallocene to MAO-treated silica is kept in the range of 2-10% by weight.

#### EXAMPLE 1

**[0034]** 7.7 mmoles of a 5:1 molar mixture of triethylaluminum (TEAL) and triisobutylaluminum (TIBAL) in 7.7 ml hexane/heptane mixture (1:3 volume ratio) were placed in a stainless steel bomb along with 0.05 mmole of cyclohexylmethyl-

dimethoxysilane (CMDS) and mixed by shaking. A mineral oil slurry of 30 mg of a conventional supported Ziegler-Natta catalyst component was introduced into the transfer bomb followed by a mineral oil slurry of 33 mg of diphenylmethyl (fluorenyl)(cyclopentadienyl)zirconium dichloride supported on MAO-treated silica prepared as described above. The contents of the transfer bomb were mixed and charged along with 750 g of propylene into a 2 liter Zipperclave reactor containing 750 g of propylene and 32 mmoles hydrogen. The reactor mixture was stirred at room temperature for 7 minutes and the temperature was increased to 60°C. The polymerization continued for one hour at 60°C. At the end of this time polymerization was terminated by rapidly venting the reactor of unreacted monomer. The polymer analysis is shown in Table I.

[0035] Molecular weight distribution (MWD) is the ratio of the weight average molecular weight ( $M_w$ ) to the number average molecular weight ( $M_n$ ):  $MWD = M_w/M_n$ . This ratio is also known as polydispersity.

[0036] Xylene solubles are measured by dissolving the polymer in hot xylene, cooling the solution to 0°C and precipitating out the isotactic form. The xylene solubles are the wt% of the polymer that was soluble in the cold xylene.

[0037] The percent SPP was determined by NMR analysis.

## EXAMPLE 2

[0038] The procedures of Example 1 were repeated except that 69 mg of the supported metallocene catalyst, 9.4 mmole of the TIBA/TEAl mixture and 0.065 mmole of CMDS were used. The polymer analysis is shown in Table I.

## EXAMPLE 3

[0039] The procedures of Example 1 were repeated except that 133 mg of the supported metallocene catalyst, 12.8 mmole of the TIBA/TEAl mixture and 0.086 mmole of CMDS were used. The polymer analysis is shown in Table I.

## EXAMPLE 4

[0040] The procedures of Example 1 were repeated except that 266 mg of the supported metallocene catalyst, 18.7 mmole TIBA/TEAl mixture and 0.125 mmole of CMDS were used. The polymer analysis is shown in Table I.

## COMPARATIVE EXAMPLE 1

[0041] The procedures of Example 1 were repeated except that only the conventional Ziegler-Natta (isospecific) catalyst was present. The polymer analysis is shown in Table I.

## COMPARATIVE EXAMPLE 2

[0042] The procedures of Example 1 were repeated except that only the supported metallocene (syndiospecific) catalyst was present. The polymer analysis is shown in Table I.

TABLE I

EXAMPLE	%sPP	MWD ( $M_w/M_n$ )	Melt Flow Index (g/10 min)	Xylene Solubles (%)
1	<2	9.0	2.9	3.6
2	2.34	9.6	4.0	4.6
3	4.0	8.2	3.5	3.9
4	13.9	8.3	4.7	5.4
Comp.Ex 1	100	2.4	3.5	3.2
Comp.Ex 2	0%	8.4	2.1	2.4

[0043] Solution blends in different ratios of pure syndiotactic and pure isotactic polymers were made and the solvent was removed. The resulting solid was analyzed for tacticity by C-13 NMR. Calibration curves were constructed using the pentad values for different blends. The composition of the reactor blends obtained from Examples 1-4 was determined by comparison of their pentad content to calibrated graphs.

[0044] The present invention provides a polymer blend having increased molecular weight distribution. As shown in Table I, the molecular weight distribution of a polymer blend having less than about 4.0% by weight of the syndiotactic

polymer, i.e., a Ti:Zr molar ratio ranging up to 0.48:1, is from 8.2 to 9.6. The molecular weight distribution of syndiotactic polypropylene alone is 2.4 and the molecular weight distribution of isotactic polypropylene alone is 8.4. Polymer blends of syndiotactic polypropylene and isotactic polypropylene have molecular weight distribution greater than either a syndiotactic homopolymer or an isotactic homopolymer. It should be noted that measurement of polydispersity can vary depending on the catalyst which produced the polymer and the instrument which is used. The molecular weight distribution of 8.2 would have an estimated variance of  $\pm 1$  and the molecular weight distribution of 9.6 would have an estimated variance of 1.5. However, since these measurements were taken on the same machine using the same procedure at or near the same time, they represent a comparison of relative values to each other.

[0045] The present invention provides a polymer blend having high xylene solubles. As shown in Table I, the xylene solubles of a polymer blend within a range from 2% by weight of syndiotactic polypropylene to 13.9% by weight, i.e., a Ti:Zr molar ratio ranging up to 0.21:1, is above 3.2%, and generally ranges from 3.4% by weight to 5.4% by weight. The percent xylene solubles of syndiotactic polypropylene alone is 3.2% and the percent xylene solubles of isotactic polypropylene alone is 2.4%. Polymer blends of syndiotactic polypropylene and isotactic polypropylene have a level of xylene solubles higher than that for either a syndiotactic homopolymer or an isotactic homopolymer.

[0046] The present invention provides a polymer blend having high melt flow. As shown in Table I, the melt flow index of a polymer blend within a range from 2.34% by weight of syndiotactic polypropylene to 13.9% by weight, i.e., a Ti:Zr molar ratio ranging from 0.8:1 to 0.21:1, is above 3.5 g/10 min, generally ranges from above 3.5 g/10 min to 4.7 g/10 min. The melt flow index of syndiotactic polypropylene alone is 3.5 g/10 min and the melt flow index of isotactic polypropylene alone is 2.1 g/10 min. Polymer blends of syndiotactic polypropylene and isotactic polypropylene have a melt flow that is higher than that for either a syndiotactic homopolymer or an isotactic homopolymer.

#### EXAMPLE 5

[0047] The film of 0.6 mil thickness was prepared in a two stage draw process. The polymer blend stabilized with 0.1 wt.% calcium stearate, 0.05 wt.% 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (tradename of American Cyanamid Company - Cyanox 1790) and 0.05 wt.% bis(2,4-di-*t*-butylphenyl)pentamerythritol diphosphite (tradename of G.E. Specialty Chemicals - Ultrinox 626). The mixture was plastified and compressed in an extruder. The melt was then extruded through a flat sheet die and brought into contact with a cooling cylinder. The polymer sheet so produced is a biaxially drawn, i.e., longitudinally and transversely with respect to the direction of extrusion, at temperatures below the melting point of the polymer blend. The draw ratio in the longitudinal direction is at least 4:1 and the product of the longitudinal and transverse draw ratios is at least about 16:1.

[0048] The clarity or haze was determined by measuring light deflected from the path of incident light due to light scattering by the haze of the sample using the XL211 Hazegard® system manufactured by Pacific Scientific.

[0049] The present invention provides a polypropylene composition for improved clarity or haze in a biaxially oriented film. The percent haze of a polymer blend within a range from less than 2.0% by weight of syndiotactic polypropylene to 13.9% by weight, i.e., a Ti:Zr molar ratio up to 0.21:1 or, more particularly, a Ti:Zr molar ratio from 1.7:1 to 0.21:1, is from 3% to 5%. The %haze of isotactic polypropylene homopolymer is 9% and of syndiotactic polypropylene homopolymer is 2%. Polymer blends of syndiotactic polypropylene and isotactic polypropylene have haze values that are better than that for an isotactic homopolymer.

[0050] Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

#### Claims

1. A polymer blend comprising a reactor blend of:

- a) isotactic polypropylene;
- b) syndiotactic polypropylene;

wherein the syndiotactic polypropylene is up to 4% by weight and wherein the molecular weight distribution is from 7.2 to 11.1

2. The polymer blend of Claim 1 wherein the syndiotactic polypropylene is less than 2% by weight.

3. A process for obtaining a reactor polymer blend comprising:

- a) allowing a conventional Ziegler-Natta catalyst component, a metallocene compound supported on silica

treated with an alumoxane and an organoaluminum compound to contact each other to form activated catalysts in a reaction zone

wherein the ratio of the conventional Ziegler-Natta catalyst component to metallocene compound as given by a Ti:Zr molar ratio ranges up to 0.48:1;

- b) introducing propylene to the reaction zone;
- c) maintaining the reaction zone at polymerization conditions;
- d) withdrawing a polymer blend of isotactic polypropylene and syndiotactic polypropylene

wherein the syndiotactic polypropylene is up to 4% by weight and wherein the molecular weight distribution is above 7.2.

4. The process of Claim 3 wherein the syndiotactic polypropylene is less than 2% by weight.

5. A biaxially oriented film comprising a reactor polymer blend of:

- a) isotactic polypropylene;
- b) syndiotactic polypropylene;

wherein the syndiotactic polypropylene is up to 13.9% by weight and wherein the percent haze of the film is less than 5%.

6. The biaxially oriented film of Claim 5 wherein the syndiotactic polypropylene is from 2.34% to 13.9% by weight.

7. The biaxially oriented film of Claim 5 wherein the percent haze is from 3% to 5%.

8. A process for obtaining a reactor polymer blend comprising:

a) allowing a conventional Ziegler-Natta catalyst component, a metallocene compound supported on silica treated with an alumoxane and an organoaluminum compound to contact each other to form activated catalysts in a reaction zone

wherein the ratio of the conventional Ziegler-Natta catalyst component to metallocene compound as given by a Ti:Zr molar ratio up to 0.21:1.

- b) introducing propylene to the reaction zone;
- c) maintaining the reaction zone at polymerization conditions;
- d) withdrawing a polymer blend of isotactic polypropylene and syndiotactic polypropylene

wherein the syndiotactic polypropylene is up to 13.9% by weight and

e) making a biaxially oriented film

wherein the percent haze of the film is less than 5%.

9. The process of Claim 8 wherein the syndiotactic polypropylene is from 2.34 to 13.9% by weight.

10. The process of Claim 8 wherein the percent haze is from 3% to 5%.

11. A polymer blend comprising a reactor blend of:

- a) isotactic polypropylene;
- b) syndiotactic polypropylene;

wherein the syndiotactic polypropylene is within a range from 2.34% by weight to 13.9% by weight and wherein the melt flow is above 3.5 g/10 min.

12. The polymer blend of Claim 11 wherein the melt flow is from above 3.5 g/10 min to 4.7 g/10 min.

13. A process for obtaining a reactor polymer blend comprising:

a) allowing a conventional Ziegler-Natta catalyst component, a metallocene compound supported on silica treated with an alumoxane and an organoaluminum compound to contact each other to form activated catalysts

in a reaction zone

wherein the ratio of the conventional Ziegler-Natta catalyst component to metallocene compound as given by a Ti:Zr molar ratio ranging from 0.8:1 to 0.21:1;

- b) introducing propylene to the reaction zone;
- c) maintaining the reaction zone at polymerization conditions;
- d) withdrawing a polymer blend of isotactic polypropylene and syndiotactic polypropylene

wherein the syndiotactic polypropylene is within a range from 2.34% by weight to 13.9% by weight and wherein the melt flow is above 3.5 g/10 min.

14. A polymer blend comprising a reactor blend of:

- a) isotactic polypropylene;
- b) syndiotactic polypropylene;

wherein the syndiotactic polypropylene is within a range from 2% by weight to 13.9% by weight and wherein the level of xylene solubles is above 3.2 % by weight.

15. The polymer blend of Claim 14 wherein the level of xylene solubles is within a range from 3.4% by weight to 5.4% by weight.

16. A process for obtaining a reactor polymer blend comprising:

- a) allowing a conventional Ziegler-Natta catalyst component, a metallocene compound supported on silica treated with an alumoxane and an organoaluminum compound to contact each other to form activated catalysts in a reaction zone

wherein the ratio of the conventional Ziegler-Natta catalyst component to metallocene compound is as given by a Ti:Zr molar ratio ranging up to 0.21:1;

- b) introducing propylene to the reaction zone;
- c) maintaining the reaction zone at polymerization conditions;
- d) withdrawing a polymer blend of isotactic polypropylene and syndiotactic polypropylene

wherein the syndiotactic polypropylene is within a range from 2% by weight to 13.9% by weight and wherein the level of xylene solubles is above 3.2 % by weight.

## Patentansprüche

1. Eine Polymermischung umfassend eine Reaktormischung aus:

- a) isotaktischem Polypropylen,
- b) syndiotaktischem Polypropylen,

wobei das syndiotaktische Polypropylen bis zu 4 Gew.% ist, und wobei die Molekulargewichtsverteilung von 7,2 bis 11,1 ist.

2. Polymermischung nach Anspruch 1, wobei das syndiotaktische Polypropylen weniger als 2 Gew.% ist.

3. Verfahren zum Erhalten einer Reaktorpolymermischung, umfassend:

- a) Ermöglichen, daß eine herkömmliche Ziegler-Natta Katalysatorkomponente, eine Metallocenverbindung, unterstützt auf Siliciumdioxid, behandelt mit einem Alumoxan, und eine Organoaluminiumverbindung miteinander unter Bilden von aktivierten Katalysatoren in einer Reaktionszone in Kontakt treten, wobei das Verhältnis der herkömmlichen Ziegler-Natta Katalysatorkomponente zur Metallocenverbindung, wie durch ein Ti:Zr Mol-verhältnis gegeben, bis zu 0,48:1 reicht,
- b) Einführen von Propylen in die Reaktionszone,
- c) Beibehalten der Reaktionszone bei Polymerisationsbedingungen,



d) Abziehen einer Polymermischung aus isotaktischem Polypropylen und syndiotaktischem Polypropylen, wobei das syndiotaktische Polypropylen bis zu 4 Gew.% beträgt, und wobei die Molekulargewichtsverteilung oberhalb von 7,2 ist.

4. Verfahren nach Anspruch 3, wobei das syndiotaktische Polypropylen geringer als 2 Gew.% ist.

5. Biaxial orientierter Film, umfassend eine Reaktorpolymermischung aus:

- a) isotaktischem Polypropylen,
- b) syndiotaktischem Polypropylen,

wobei das syndiotaktische Polypropylen bis zu 13,9 Gew.% beträgt, und wobei die Prozente Trübung des Films geringer als 5% sind.

6. Biaxial orientierter Film nach Anspruch 5, wobei das syndiotaktische Polypropylen von 2,34 Gew.% bis 13,9 Gew.% beträgt.

7. Biaxial orientierter Film nach Anspruch 5, wobei die Prozente Trübung von 3% bis 5% sind.

8. Verfahren zum Erhalten einer Reaktorpolymermischung umfassend:

- a) Ermöglichen, daß eine herkömmliche Ziegler-Natta Katalysatorkomponente, eine Metallocenverbindung, unterstützt auf Siliciumdioxid, behandelt mit einem Alumoxan, und eine Organoaluminiumverbindung miteinander unter Bilden aktivierter Katalysatoren in einer Reaktionszone in Kontakt treten, wobei das Verhältnis der herkömmlichen Ziegler-Natta Katalysatorkomponente zur Metallocenverbindung, wie durch ein Ti:Zr Mol-verhältnis gegeben, bis zu 0,21:1 beträgt,
- b) Einführen von Propylen in die Reaktionszone,
- c) Beibehalten der Reaktionszone bei Polymerisationsbedingungen,
- d) Abziehen einer Polymermischung aus isotaktischem Polypropylen und syndiotaktischem Polypropylen, wobei das syndiotaktische Polypropylen bis zu 13,9 Gew.% beträgt, und
- e) Herstellen eines biaxial orientierten Films, wobei die Prozente Trübung des Films geringer als 5% sind.

9. Verfahren nach Anspruch 8, wobei das syndiotaktische Polypropylen von 2,34 Gew.% bis 13,9 Gew.% beträgt.

10. Verfahren nach Anspruch 8, wobei die Prozente Trübung von 3% bis 5% sind.

11. Polymermischung, umfassend eine Reaktormischung aus

- a) isotaktischem Polypropylen,
- b) syndiotaktischem Polypropylen,

wobei das syndiotaktische Polypropylen in einem Bereich von 2,34 Gew.% bis 13,9 Gew.% ist, und wobei der Schmelzfluß oberhalb von 3,5 g/10 Min ist.

12. Polymermischung nach Anspruch 11, wobei der Schmelzfluß oberhalb von 3,5 g/10 Min bis 4,7 g/10 Min liegt.

13. Verfahren zum Erhalten einer Reaktorpolymermischung, umfassend:

- a) Ermöglichen, daß eine herkömmliche Ziegler-Natta Katalysatorkomponente, eine Metallocenverbindung, unterstützt auf Siliciumdioxid, behandelt mit einem Alumoxan, und eine Organoaluminiumverbindung miteinander unter Bilden von aktivierten Katalysatoren in einer Reaktionszone in Kontakt treten, wobei das Verhältnis der herkömmlichen Ziegler-Natta Katalysatorkomponente zur Metallocenverbindung, wie durch ein Ti:Zr Mol-verhältnis gegeben, im Bereich von 0,8:1 bis 0,21:1 ist,
- b) Einführen von Propylen in die Reaktionszone,
- c) Beibehalten der Reaktionszone bei Polymerisationsbedingungen,
- d) Abziehen einer Polymermischung aus isotaktischem Polypropylen und syndiotaktischem Polypropylen, wobei das syndiotaktische Polypropylen in einem Bereich von 2,34 Gew.% bis 13,9 Gew.% ist, und wobei der

Schmelzfluß oberhalb von 3,5 g/10 Min ist.

14. Polymermischung, umfassend eine Reaktormischung aus:

- a) isotaktischem Polypropylen,
- b) syndiotaktischem Polypropylen,

wobei das syndiotaktische Polypropylen in einem Bereich von 2 Gew.% bis 13,9 Gew.% liegt, und wobei der Spiegel von xylollöslichen Stoffen oberhalb von 3,2 Gew.% liegt.

15. Polymermischung nach Anspruch 14, wobei der Spiegel von xylollöslichen Stoffen in einem Bereich von 3,4 Gew.% bis 5,4 Gew.% ist.

16. Verfahren zum Erhalten einer Reaktorpolymermischung, umfassend:

- a) Ermöglichen, daß eine herkömmliche Ziegler-Natta Katalysatorkomponente, eine Metallocenverbindung, unterstützt auf Siliciumdioxid, behandelt mit einem Alumoxan, und eine Organoaluminiumverbindung miteinander unter Bilden von aktivierten Katalysatoren in einer Reaktionszone in Kontakt treten, wobei das Verhältnis der herkömmlichen Ziegler-Natta Katalysatorkomponente zur Metallocenverbindung so ist, wie durch ein Ti:Zr Molverhältnis gegeben, das bis zu 0,21:1 reicht,
- b) Einführen von Propylen in die Reaktionszone,
- c) Beibehalten der Reaktionszone bei Polymerisationsbedingungen,
- d) Abziehen einer Polymermischung aus isotaktischem Polypropylen und syndiotaktischem Polypropylen, wobei

das syndiotaktische Polypropylen in einem Bereich von 2 Gew.% bis 13,9 Gew.% liegt, und wobei der Spiegel von xylollöslichen Stoffen oberhalb von 3,2 Gew.% liegt.

## Revendications

1. Un mélange de polymères comprenant un mélange dans un réacteur de:

- a) un polypropylène isotactique;
- b) un polypropylène syndiotactique;

dans lequel le polypropylène syndiotactique constitue jusqu'à 4% en poids et où la répartition des poids moléculaires est de 7,2 à 11,1.

2. Le mélange de polymères selon la revendication 1 dans lequel le polypropylène syndiotactique est inférieur à 2% en poids.

3. Un procédé pour obtenir un mélange de polymères dans un réacteur comprenant:

- a) permettre la mise en contact d'un composant habituel de catalyseur de Ziegler-Natta, un composé de métallocène sur support de silice traité avec un alumoxane et un composé d'organoaluminium les uns avec les autres pour former des catalyseurs activés dans la zone de réaction où le rapport du composant habituel de catalyseur de Ziegler-Natta à composé de métallocène exprimé par le rapport molaire de Ti:Zr s'élève jusqu'à 0,48:1;

- b) introduire le propylène dans la zone de réaction;
- c) maintenir la zone de réaction aux conditions de polymérisation;
- d) retirer un mélange de polymères de polypropylène isotactique et de polypropylène syndiotactique dans lequel le polypropylène syndiotactique constitue jusqu'à 4% en poids et dans lequel la répartition des poids moléculaires est supérieure à 7,2.

4. Procédé selon la revendication 3 dans lequel le polypropylène syndiotactique est inférieur à 2% en poids.

5. Un film orienté biaxialement comprenant un mélange de polymères dans réacteur de:

- a) un polypropylène isotactique;
- b) un polypropylène syndiotactique;

dans lequel le polypropylène syndiotactique constitue jusqu'à 13,9% en poids et dans lequel le pourcentage d'opacité du film est inférieur à 5%.

6. Le film biaxialement orienté de la revendication 5, dans lequel le polypropylène syndiotactique constitue de 2,34% à 13,9% en poids.

7. Le film biaxialement orienté selon la revendication 5, dans lequel le pourcentage d'opacité se situe de 3% à 5% en poids.

8. Un procédé pour obtenir un mélange de polymères dans un réacteur comprenant:

a) permettre la mise en contact d'un composant habituel de catalyseur de Ziegler-Natta, un composé de métallocène sur support de silice traité avec un alumoxane et un composé d'organoaluminium les uns avec les autres pour former des catalyseurs activés dans la zone de réaction

où le rapport du composant habituel de catalyseur de Ziegler-Natta à composé de métallocène exprimé par le rapport molaire de Ti:Zr s'élève jusqu'à 0,21:1;

b) introduire le propylène dans la zone de réaction;

c) maintenir la zone de réaction aux conditions de polymérisation;

d) retirer un mélange de polymères de polypropylène isotactique et de polypropylène syndiotactique dans lequel le polypropylène syndiotactique constitue jusqu'à 13,9% en poids et

e) réaliser un film orienté biaxialement où le pourcentage d'opacité du film est inférieur à 5%.

9. Procédé selon la revendication 8 dans lequel le polypropylène syndiotactique se situe entre 2,34 à 13,9% en poids.

10. Le procédé selon la revendication 8, dans lequel le pourcentage d'opacité se situe de 3% à 5% en poids.

11. Un mélange de polymères comprenant un mélange dans un réacteur de:

- a) un polypropylène isotactique;
- b) un polypropylène syndiotactique;

où le polypropylène syndiotactique se situe dans un intervalle de 2,34% en poids à 13,9% en poids et où l'indice de fusion est supérieur à 3,5g/10min.

12. Le mélange de polymères selon la revendication 11 dans lequel l'indice de fusion est supérieur à 3,5g/10min à 4,7g/10min.

13. Un procédé pour obtenir un mélange de polymères dans un réacteur comprenant:

a) permettre la mise en contact d'un composant habituel de catalyseur de Ziegler-Natta, un composé de métallocène sur support de silice traité par un alumoxane et un composé d'organoaluminium les uns avec les autres pour former des catalyseurs activés dans une zone de réaction

où le rapport du composant habituel de catalyseur de Ziegler-Natta à composé de métallocène exprimé par le rapport molaire de Ti:Zr se situe de 0,8:1 à 0,21:1;

b) introduire le propylène dans la zone de réaction;

c) maintenir la zone de réaction aux conditions de polymérisation;

d) retirer un mélange de polymères de polypropylène isotactique et de polypropylène syndiotactique

dans lequel le polypropylène syndiotactique se situe dans un intervalle de 2,34% en poids à 13,9% en poids et dans lequel l'indice de fusion est supérieur à 3,5g/10min.

14. Un mélange de polymères comprenant un mélange dans un réacteur de:

- a) un polypropylène isotactique;
- b) un polypropylène syndiotactique;

dans lequel le polypropylène syndiotactique se trouve dans un intervalle de 2% en poids à 13,9% en poids et dans lequel le niveau de matières solubles dans le xylène est supérieur à 3,2% en poids.

5 15. Le mélange de polymères selon la revendication 14 dans lequel le niveau de matières solubles dans le xylène est dans un intervalle de 3,4% à 5,4% en poids.

16. Un procédé pour obtenir un mélange de polymères dans un réacteur comprenant:

10 a) permettre la mise en contact d'un composant habituel de catalyseur de Ziegler-Natta, un composé de métallocène sur support de silice traité avec un alumoxane et un composé d'organoaluminium les uns avec les autres pour former des catalyseurs activés dans une zone de réaction dans lequel le rapport du composant habituel de catalyseur de Ziegler-Natta à composé de métallocène exprimé en rapport molaire de Ti:Zr s'élève jusqu'à 0,21:1;

15 b) introduire le propylène dans la zone de réaction;

c) maintenir la zone de réaction aux conditions de polymérisation;

d) retirer un mélange de polymères de polypropylène isotactique et de polypropylène syndiotactique

20 dans lequel le polypropylène syndiotactique se situe dans un intervalle de 2% en poids à 13,9% en poids et dans lequel le niveau de matières solubles dans le xylène est supérieur à 3,2% en poids.